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(54) EPOXY RESIN COMPOSITION

(57)Abstract:
PURPOSE: To obtain an epoxy resin composition useful for protecting semiconductors, having extremely improved reliability of a transparent sealing material, comprising specific inorganic complex oxide particles and an epoxy resin, making the refractive indexes of the particles and the epoxy resin satisfy a specific value.
CONSTITUTION: The objective composition comprises (A) inorganic complex oxide particles (silica-coated inorganic oxide particles prepared by coating the surface of inorganic complex oxide particles preferably with silica) having ≤9 × 10−6 surface hydroxyl group density and an epoxy resin and the refractive index (NFD) of the inorganic complex oxide particles and the refractive index (NPD) of the cured material of the epoxy resin satisfy the formula. When the material is cured, a cured material having ≥50% light transmittance at 589nm is obtained.

$$|N_{FD} - N_{PD}| \leq 0.010$$

CLAIMS

[Claim(s)]

[Claim 1]Surface-water-of-aggregate acid radical density contains inorganic compound oxide particles and an epoxy resin which are below the 9x10 $^{-6}$ equivalent / m^2, And an epoxy resin composition, wherein a refractive index ($N^F{}_D$) of inorganic compound oxide particles and a refractive index ($N^P{}_D$) of a cured body of an epoxy resin satisfy a following formula.

$| N^F{}_D-N^P{}_D| <= 0.010$ [Claim 2]The epoxy resin composition according to claim 1 whose inorganic compound oxide particles are the silica covering inorganic matter compound oxide particles which covered the inorganic compound-oxide-particles surface with silica.

[Claim 3]A transparency cured body which hardens the epoxy resin composition according to claim 1, and is characterized by transmissivity of 589-nm light being not less than 50%.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the transparent sealing agent for protecting optical semiconductors, such as a light emitting device and a photo detector, from the external world. In detail, it is related with the epoxy resin composition which consists of an inorganic multiple oxide and an epoxy resin, and its cured body.
[0002]
[Description of the Prior Art]Conventionally, it excelled in mechanical properties and electrical insulation, the adhesive property of an epoxy resin is high, and since it moreover has the features, like there is little contraction at the time of hardening, it has been widely used as an IC package. However, high physical properties, such as moisture resistance and heat resistance, came to be searched for with high integration of a circuit. Then, in order to aim at improvement in the heat resistance of an epoxy resin, or damp-proof physical properties, generally addition of inorganic fillers, such as alumina and silica, has been performed. For example, it is indicated by JP,2-26313,A, JP,2-145415,A, JP,2-145416,A, and JP,2-158637,A by being filled up with spherical silica that a low thermal expansion coefficient and the resin composition for sealing agents of high moisture resistance are obtained.
[0003]
[Problem(s) to be Solved by the Invention]On the other hand, in recent years, progress of an opto-electronics pertinent art is remarkable, and, in addition to the above-mentioned physical properties, transparency was able to come to ask closure of the optical semiconductor. However, the cured body of the epoxy resin which composite-ized the above-mentioned inorganic filler is almost opaque, and is not suitable for the sealing agent of an optical semiconductor.
[0004]The epoxy resin composition which does not contain an inorganic filler as a transparent sealing agent is proposed variously. However, a coefficient of thermal expansion is high, and since a heat-resistant and damp-proof problem is not solved, either, development of the transparent sealing agent containing an inorganic filler is desired.
[0005]The epoxy resin composition using the inorganic filler which has a specific refractive index as what responds to this is proposed. Although the composite metal oxide which uses silica as a base was used as such a filler, in spite of having added the filler in this case, neither the moisture resistance of a cured body nor glass transition temperature was enough, and exfoliation between an element and a sealing agent and the problem of the package crack were left behind. Since it turned yellow at the time of hardening, there was a problem that light transmittance fell.
[0006]
[Means for Solving the Problem]This invention persons by covering the surface of reducing surface-water-of-aggregate acid radical density of an inorganic filler, and also an inorganic filler with silica, as a result of inquiring wholeheartedly that an aforementioned problem should be solved about a transparent sealing agent containing an inorganic filler, The moisture resistance of a cured body and glass transition temperature improve, and also it finds out that yellowing at the time of hardening decreases, and came to complete this invention.
[0007]Namely, this invention contains inorganic compound oxide particles and an epoxy resin whose surface-water-of-aggregate acid radical density is below the 9×10^{-6} equivalent / m^2, And a refractive index (N^F_D) of inorganic compound oxide particles and a refractive index (N^P_D) of a cured body of an epoxy resin are the

epoxy resin compositions satisfying a following formula.
[0008]| An invention of $N^F_D-N^P_D$|<=0.010 others is a transparency cured body which hardens this epoxy resin composition and is characterized by transmissivity of 589-nm light being not less than 50%.
[0009]Inorganic compound oxide particles of this invention will be adopted without limiting especially publicly known inorganic compound oxide particles or glass particles, if a refractive index (N^F_D) after adjustment of surface-water-of-aggregate acid radical density fills the above-mentioned formula. In order for a cured body of an epoxy resin composition containing inorganic compound oxide particles obtained eventually to hold transparency, it is necessary to combine a refractive index of these particles with it of an epoxy resin cured body mentioned later, and to dedicate it in a mentioned range. A presentation of inorganic compound oxide particles will not be restricted especially if the target refractive index is obtained. As an ingredient of suitable inorganic compound oxide particles, a multiple oxide which makes silica one ingredient is mentioned especially. ********** from a group which will consist of the 2nd fellows of the periodic table in whom silica and silica, and composite-izing (combination) are possible, the 3rd fellows, and the 4th fellows if a suitable multiple oxide is illustrated especially -- even if small, it is a multiple oxide which consists of a kind of metallic oxide. If the above-mentioned metallic oxide is illustrated concretely, magnesium oxide, a calcium oxide, strontium oxide, barium oxide, boron oxide, an aluminum oxide, titanium oxide, zirconium oxide, oxidation hafnium, tin oxide, a zinc oxide, etc. are typical. These multiple oxides are combined via silicon and oxygen of silica. Although a rate in particular of silica in the above-mentioned multiple oxide is not restricted, when 80-95-mol% of a thing attains the purpose of this invention, it is preferred preferably 60-99-mol% especially.
[0010]As for adjustment of a refractive index of inorganic compound oxide particles of this invention, it is common to carry out by changing a kind of metallic oxide compounded with silica and a ratio. In this case, it is preferred to use especially an oxide whose refractive index is higher than silica, such as strontium oxide, oxidation titanium, zirconium oxide, oxidation hafnium, and tin oxide. A manufacturing method of the above-mentioned inorganic compound oxide particles is adopted that a publicly known method does not especially have restriction. For example, there are a sol-gel method, the grinding-classifying method, a coprecipitation method, etc. If a typical manufacturing method is illustrated especially, after mixing an alkoxide of metal, such as alkoxysilane hydrolyzed selectively, titanium, or a zirconium, there is a sol-gel method dropped while agitating this mixed solution to an alkaline alcohol solution. In this case, a refractive index of inorganic powder obtained can be adjusted by adjusting a quantitative ratio of a starting material.
[0011]Inorganic compound oxide particles whose surface-water-of-aggregate acid radical density is below the 9×10^{-6} equivalent / m^2 adjust quantity of a hydroxyl group of the above-mentioned inorganic compound-oxide-particles surface. When surface-water-of-aggregate acid radical density of inorganic compound oxide particles exceeds the 9×10^{-6} equivalent / m^2, the moisture resistance of an epoxy resin composition cured body produced by carrying out mixing postcure to an epoxy resin is bad, and glass transition temperature does not improve. Although surface-water-of-aggregate acid radical density is so preferred that it is low, at present, a degree of sintering and crystalline ****** of particles which are described below can be obtained to a thing about the 6×10^{-6} equivalent / m^2 on balance with cooking temperature of particles which have on the transparency of a cured body.
[0012]A method publicly known for reducing hydroxyl group density of the surface is employable without restriction. For example, there is a method of heat-treating as a typical method. Cooking temperature can be arbitrarily chosen, if it is a range which particles do not sinter and inorganic compound oxide particles do not crystallize. If temperature is too high, in order for inorganic compound oxide particles to crystallize or to sinter, the transparency of an epoxy resin composition cured body falls. If cooking temperature is too low, surface-water-of-aggregate acid radical density of inorganic compound oxide particles cannot be lowered. Then, 900-1200 ** of cooking temperature is preferred, and its 950-1100 ** is more preferred. Time which heating takes can be arbitrarily chosen, if it is a range which inorganic compound oxide particles do not crystallize.
[0013]In this invention, although mean particle diameter in particular of inorganic compound oxide particles is not limited, light transmittance used as an index of the transparency of an epoxy resin composition cured body is so high that mean particle diameter is small. For this reason, 20 micrometers or less of mean particle diameter are preferred, and its 0.04-5 micrometers are more preferred. The above-mentioned inorganic particle may mix and use two or more sorts of things from which mean particle diameter differs. The transparency of an epoxy resin composition hardened as above-mentioned, so that mean particle diameter was small is high, and

since temperature dependence will appear in the transparency of a cured body if mean particle diameter becomes large, when using in a part accompanied by generation of heat etc., it is preferred to use what has small mean particle diameter.

[0014]Although shape in particular of inorganic compound oxide particles is not restricted, when it mixes with an epoxy resin, in order to obtain a constituent excellent in mobility, its spherical thing is preferred.

[0015]A publicly known method is employable as a manufacturing method of silica covering inorganic matter compound oxide particles which covered the surface of inorganic compound oxide particles with silica without restriction. For example, tetraethyl silicate is dropped at liquid which made an alkaline alcohol solution distribute inorganic composite metal oxide particles, and there is a method of depositing hydrolyzate of tetraethyl silicate on the surface of inorganic compound oxide particles. Thickness of a silica enveloping layer of silica covering inorganic matter compound oxide particles can be arbitrarily chosen, if it is a range to which the transparency of a cured body of an epoxy resin composition which consists of these silica covering inorganic matter compound oxide particles and an epoxy resin does not fall. As this thickness, 1-30 nm is preferred and 3-15 nm is more preferred, for example. Adjustment of thickness of an enveloping layer is performed by adjusting a ratio of quantity of a raw material of silica used for covering, and specific surface area of inorganic compound oxide particles. Although it can also ask for measurement of the thickness by calculation from brewing composition ratio, it is performed by observation of a transmission electron microscope photograph depending on a presentation. After a sample for transmission electron microscope observation carries out embedding of the silica covering inorganic matter compound oxide particles of this invention to resin, such as acrylate or epoxy, it can be ground and can observe a section of particles, for example.

[0016]Silica covering inorganic matter compound oxide particles produced by making it above are heated in order to remove moisture, an organic matter, etc. which are contained in particles and to prepare surface-water-of-aggregate acid radical density to below the 9×10^{-6} equivalent / m^2 (temporary quenching). Although it is not limited, when sintering of particles, etc. are taken into consideration, as for especially temporary-quenching temperature, 900-1200 ** is preferred, and it is more preferred. [of 950-1100 **] Although temporary-quenching time in particular is not limited, 30 minutes - 10 hours are preferred.

[0017]Generally, when mean particle diameter heat-treats a multiple oxide particle of 1 micrometer or less at a not less than 1000 ** elevated temperature, it is in a tendency for particles to sinter and for the monodisperse nature of particles to fall. Like silica covering inorganic matter compound oxide particles of this invention, if the surface of inorganic compound oxide particles is chemically covered with inertness silica, even if it heat-treats at a not less than 1000 ** elevated temperature, a thing excellent in monodisperse nature will be obtained.

[0018]A refractive index ($N^F{}_D$) of silica covering inorganic matter multiple oxide particles of this invention also needs to fill an expression of relations with a refractive index ($N^P{}_D$) of said epoxy resin cured body. If silica is covered to inorganic compound oxide particles, according to thickness of a silica enveloping layer, a refractive index of silica covering inorganic matter compound oxide particles will fall. Therefore, as for a refractive index of inorganic compound oxide particles, it is more preferred than a target refractive index beforehand to set up more highly.

[0019]Measurement of a refractive index can be performed with an immersion method using an Abbe refractometer so that a postscript may be carried out.

[0020]Surface-water-of-aggregate acid radical density used by this invention inorganic compound oxide particles which are below the 9×10^{-6} equivalent / m^2, Since the stability of description of particles is improved further and dispersibility to an epoxy resin is raised, processing agents, such as an organic silicon compound and an organic titanium compound, can perform a surface treatment. After this processing contacts a solvent which dissolved a processing agent, and inorganic compound oxide particles, it is common to remove this solvent. As an organic silicon compound of a processing agent, alkoxy silane compounds, such as gamma-glycidoxypropyltrimetoxysilane, gamma-methacryloxpropyl trimethoxy silane, and vinyltriethoxysilane, are preferred, and especially a thing that has an epoxy group especially is preferred. applying an ultrasonic wave, after distributing solutions, such as water, alcohol, and acetone, when compound oxide particles are condensing after the above-mentioned surface treatment — or it is preferred to solve condensation of particles with a grinding machine etc.

[0021]Inorganic compound oxide particles prepared as mentioned above knead with an epoxy resin, and an epoxy resin composition is prepared.

[0022]As an epoxy resin used by this invention, a publicly known thing is especially adopted without restriction. For example, a bisphenol A type epoxy resin, phenol novolak type epoxy resin, Cycloaliphatic epoxy resin, a heterocycle type epoxy resin, glycidyl ester typed epoxy resin, Epoxy resin compositions, such as glycidyl amine type epoxy resin and a halogenation epoxy resin, are used as a basic component, and what blended a hardening agent, a diluent, a plasticity grant agent, fire retardant, an ultraviolet ray absorbent, paints, etc. with this if needed is mentioned.
[0023]The above-mentioned hardening agent advances a polymerization and bridge construction of an epoxy resin, and a publicly known thing is especially used without restriction. For example, acid anhydrides, such as tetrahydro phthalic anhydride, phthalic anhydride, pyromellitic dianhydride, and anhydrous methyl NAJIKKU acid, are mentioned. Loadings of the above-mentioned hardening agent are adopted that a public domain does not especially have restriction. It is preferred to use a hardening agent generally, so that it may become the range of 0.5-1.5 Eq by carboxyl group conversion to 1 Eq of epoxy groups of said epoxy resin composition.
[0024]What also has a publicly known hardening accelerator is especially used without restriction. For example, imidazole compounds, such as 2-methylimidazole, 2, 4-JIHIDORAJINO 6-methylamino S-triazine, and 2-ethyl-4-methylimidazole, boron fluoride, onium salt, etc. are mentioned. As for these hardening accelerators, a kind or two sorts or more are used if needed. Loadings of the above-mentioned hardening accelerator are adopted that a public domain does not especially have restriction. Generally, it is preferred to use it 0.1 to 8% of the weight to the total quantity of said epoxy resin composition and a hardening agent.
[0025]moreover -- when an epoxy resin is hyperviscosity, workability, defoaming nature, and a filler are [diluent] damp -- etc. -- it is added in order to improve, and a publicly known thing is especially used without restriction. For example, poly epoxy reactive diluents, such as mono- epoxy reactive diluents, such as olefin oxide, octylene oxide, and styrene oxide, butadiene dioxide, dimethylenepentane dioxide, and diethylene-glycol diglycidyl ether, etc. are mentioned. Loadings of the above-mentioned diluent are adopted that a public domain does not especially have restriction.Generally, it is used at 1 to 50 % of the weight to said epoxy resin composition.
[0026]What also has publicly known fire retardant is especially used without restriction. For example, tetrabromobisphenol A, tris (2, 3-dibromopropyl) phosphate, tricresyl phosphate, etc. are mentioned. What is necessary is just to add loadings of the above-mentioned fire retardant in the range which does not affect an effect of this invention out of a public domain.
[0027]In this invention, a rate of inorganic compound oxide particles in an epoxy resin composition is 30 to 80 % of the weight preferably 20 to 90% of the weight. When a rate of an inorganic particle is less than 20 % of the weight, the moisture resistance of a cured body of an epoxy resin composition, heat resistance, etc. are not enough, and when this rate exceeds 90 % of the weight, the mobility of an epoxy resin composition and handling nature fall.
[0028]In this invention, a mixing method in particular of inorganic compound oxide particles and an epoxy resin is not limited, but a publicly known method is adopted without restriction. For example, a method of kneading, while applying a share under a room temperature or heating using an automatic grinding machine, a kneader, a mortar, attritor, a roller, an extruder, etc. is preferred.
[0029]Generally before hardening, an epoxy resin composition of this invention is paste state, powder, or a solid state in order to use inorganic compound oxide particles and an epoxy resin as the main ingredients. That is, generally a resin composition obtained when a liquefied epoxy resin is used at a room temperature is paste state, and when an epoxy resin of paste state or a solid state is used at a room temperature, a resin composition obtained is powder, granularity, or a solid state.
[0030]In an epoxy resin composition of this invention, when an oxide particle exists by a state of aggregation in an epoxy resin, a fall of the transparency of a cured body obtained may be caused. Therefore, as for floc in a constituent, it is preferred to solve condensation as much as possible with the above-mentioned mixing method etc. Since air bubbles which exist in a cured body of an epoxy resin composition also become the cause of reducing the transparency of resin, it is preferred to remove air bubbles.
[0031]An epoxy resin composition of this invention is stiffened by a usual method, and it deals in it. If suitable curing conditions are illustrated especially, a method of heating at temperature of 80-150 ** for 2 to 30 hours can list under application of pressure or ordinary pressure, and it is ****.
[0032]Light transmittance with a wavelength of 589 nm of a transparency cured body of this invention is not less than 50%. Light transmittance is the value which measured transmissivity of light with a wavelength of 589 nm about a 1-mm-thick charge of a tabular material, as an example describes. The above-mentioned value says

a value which amended a numerical value by this absorption, when a cured body contains wavelength whose absorption wavelength of these paints is the above-mentioned 589 nm, including paints.

[0033]A refractive index of a cured body of inorganic compound oxide particles and an epoxy resin had the most transparent case where it has refractive index difference within the limits of specification as indicated to Japanese Patent Application No. 2-415291 with an epoxy resin composition using the conventional inorganic multiple oxide. As this reason, a low refractive index layer was produced in an interface of inorganic compound oxide particles and an epoxy resin, and it was presumed that this low refractive index layer neutralized refractive index difference of inorganic compound oxide particles and an epoxy resin. However, with an epoxy resin composition of this invention, transparency with a high cured body is shown, so that a value of a refractive index of inorganic compound oxide particles and an epoxy resin whose surface-water-of-aggregate acid radical density is below the 9×10^{-6} equivalent / m^2 is near. As this cause, it guesses as follows. That is, reduction or since it disappeared, a low refractive index layer produced in an interface of particles and an epoxy resin in an epoxy resin composition of this invention since the surface of particles to be used is inertness compared with particles of Japanese Patent Application No. 2-415291 can think, and it is ****.

[0034]Few cured bodies of this invention have quantity of air bubbles to contain, and so preferred a quantity of floc that there are.

[0035]

[Effect of the Invention]Although there was a problem of turning yellow at the time of hardening when the glass transition temperature with low moisture resistance whose water absorption of the cured body of the compound resin (transparent sealing agent) which consists of silica system compound oxide particles to which the conventional refractive index was adjusted, and an epoxy resin is high is low, In this invention, the above-mentioned problem was solved by reduction of surface-water-of-aggregate acid radical density, and also covering of the silica layer to the surface of particles.

[0036]It is thought of for a cured body to become difficult to incorporate moisture by reducing surface-water-of-aggregate acid radical density that the moisture resistance of the cured body improved.

[0037]The cause of improvement in glass transition temperature is guessed as follows, although it is not in **. Conventionally, when kneading an inorganic particle and an epoxy resin, the hydroxyl group of the surface of an inorganic particle reacted to the epoxy resin, the viscosity of the epoxy resin composition rose locally, and the hardening reaction of the epoxy resin did not fully advance. However, by reducing the hydroxyl group density of the surface, the reaction in an interface decreases and a hardening reaction came to advance to homogeneity more. Or very small hole or rugged surface exists in the surface of the compound oxide particles in an epoxy resin composition. This unevenness tended to produce an opening in the epoxy resin composition, and that void had lowered the glass transition temperature of the epoxy resin composition. However, by covering lowering the hydroxyl group density of the surface, and also a particle surface with silica, the surface of the inorganic particle became smooth, this void decreased, and glass transition temperature improved. Although the cause by which yellowing of the cured body decreased is not clear, either, it thinks as follows. By the conventional compound oxide particles, since activity [surface], a catalysis of some kind is caused, and it is thought that some resin oxidized to hardening reaction time. By having been covered with silica, the compound-oxide-particles surface becomes inertness and the surface of compound oxide particles is considered that oxidation reaction of resin like [former] becomes difficult to occur.

[0038]As mentioned above, since the transparency cured body of this invention had physical properties outstanding compared with the transparent sealing agent containing the conventional inorganic filler, its reliability of the transparent sealing agent improved substantially.

[0039]

[Example]Hereafter, although an example explains this invention concretely, this invention is not limited to these examples. Various measurement was performed by the following method in the example and the comparative example.

[0040](1) Mean particle diameter (mean particle diameter)

After distributing particles in ammonia nature methanol, particle size distribution was measured with the particle-size-distribution plan (made by Otsuka Electronics).

[0041](2) The refractive-index sample of particles was made suspended in the liquid in which refractive indicees differ, and the refractive index of liquid in case suspension looks transparent was measured with the Abbe's refractometer.

[0042](3) The surface-water-of-aggregate acid radical density inorganic matter compound oxide particles of particles were heated at 300 ** for 3 hours, and the water of adsorption was removed. Weight of the particles at this time is made into W_1. Then, when heated at 1000 ** for 1 hour, the elimination reaction of water occurred from inorganic compound oxide particles, and the weight of particles became W_2. The Carl Phi Shah water measurement device with a heating furnace (Mitsubishi Kasei industrial company make, CA-02) performed measurement of W_1 and W_2. It asked for the hydroxyl group density per unit area (10^{-6} equivalent / m^2) from W_1 obtained above, W_2, and the value of specific surface area (Sg).

[0043](4) The specific surface area Sg (m^2/g) of inorganic compound oxide particles required to ask for the surface-water-of-aggregate acid radical density of the specific surface area particles of particles was determined with the BET specific surface area meter (the Shimadzu make, flow soap 2100).

[0044](5) Denture packing of the epoxy resin composition before hardening was carried out to the mold which adjusted the distance between the glass plates of two light transmittance of a cured body to 4 mm with the spacer, it heated at 2 hours and also 155 ** at 100 ** for 3 hours, and the cured body of the tabular epoxy resin composition was obtained at 4 mm in thickness inserted into the glass plate. The light transmittance of this cured body was measured with the spectrophotometer (the Hitachi make, U-3210), without removing from a glass plate. The baseline was amended from the light transmittance of the glass plate of two sheets.

[0045](6) A cylindrical cured body the glass transition temperature (Tg) of a cured body and coefficient-of-linear-expansion 20 mm in length, and 4 mm in diameter was produced, and the coefficient of linear expansion was calculated with a thermomechanometry device (the product made from the Rigaku electrical machinery, Thermoflex) from the heating rate of 4 ** / min, and the measurement result in measurement temperature requirement; room temperature -200 **. Glass transition temperature (Tg) was made into the temperature which shows the folding point of expansion per unit temperature of a sample.

[0046](7) Boiling water absorption (water absorption)

A 30x15x4-mm cured body was used as the specimen, and it saved by boiling underwater for 20 hours. From the weight before and behind boiling underwater preservation, it asked with the following formula.

[0047]

[Equation 1]A= {(Wb-Wa) /Wa} x100A: Boiling water absorption (%)

Wa: Weight (g) of the specimen before saving boiling underwater

Wb: Weight (g) of the specimen after saving boiling underwater

Example 30.6 g of 1 tetraethyl silicate (trade name: the ethyl silicate 28, made in Col Coat) was melted in 120 ml of methanol. After adding 1.3 ml of chloride (0.036 % of the weight of concentration) in this solution, it held at 35 ** for 1 hour. The solution which melted 15.0 g of titaniumtetrabutoxide (made by Nippon Soda Co., Ltd.) in 100 ml of isopropanol at this was added, and the compound alkoxide solution which consists of silicon and titanium was prepared. Next, the ammonia nature alcohol solution which comprises 700 ml of methanol, 500 ml of normal butanol, and a 250-ml ammonia solution (25 % of the weight of concentration) was put into glass reactors with a content volume [with agitating blades] of 3 l., and the reaction vessel was prepared. It was dropped having covered the solution of the complex alkoxide which consists of silicon prepared previously and titanium over the reaction vessel for about 4 hours keeping the temperature of a reaction vessel at 35 **. Reaction mixture became opalescence in about 30 minutes after the dropping start. The solution which melted the tetraethyl silicate 15.2g in 40 ml of methanol was dropped at the reaction vessel in 1 hour after [after the end of dropping, and also] continuing churning for 30 minutes. After stirring reaction mixture for further 1 hour, the solvent of reaction mixture was removed by the evaporator, temporary quenching was carried out at 1000 ** for 1 hour, and silica covering inorganic matter compound oxide particles (J-1) were obtained.

[0048]Silica covering inorganic matter compound oxide particles (J-1) were the mean-particle-diameter [of 0.08 micrometer], refractive-index 1.539, 7-nm [of the coating membrane by which brewing twist presumption is carried out / in thickness], and surface-water-of-aggregate acid radical density 8.5x10 $^{-6}$ equivalent / m^2.

[0049]To the bisphenol A type epoxy resin 1g, next, 0.80 g of anhydrous 4-methyl hexahydrophthalic acid, And 4.2 mg of 2-methyl 4-imidazole and 2.5 g of silica covering inorganic matter compound oxide particles (J-1) were added, it mixed for about 40 minutes with the mortar, and the paste state epoxy resin composition which contains silica covering inorganic matter compound oxide particles (J-1) 56% of the weight was obtained. Applying an ultrasonic wave, it maintained at the vacuum for 30 minutes, and this constituent was defoamed.

Subsequently, the application-of-pressure polymerization (110 **, 12 hours) was poured in and carried out to the predetermined mold made from Teflon, and the cured body was obtained. The refractive index of the cured body of what mixed 0.80 g of anhydrous 4-methyl hexahydrophthalic acid and 4.2 mg of 2-methyl 4-imidazole to the bisphenol A type epoxy resin 1g was 1.540.
[0050]The obtained cured bodies (A) were Tg120 **, a coefficient of thermal expansion of 28 ppm/**, and 1.18% of water absorption 56 % of the weight of filler content, 55% (450 nm) of light transmittance, and 87% (589 nm).
[0051]130.9 g of example 2 tetramethyl silicate (trade name: the methylsilicate 39, made in Japanese Col Coat) was melted in the methanol 55g. After adding 7.7 g of chloride (0.036 % of the weight of concentration) in this solution, it stirred for about 10 minutes. The solution which melted 48.7 g of titaniumtetrabutoxide (made by Nippon Soda Co., Ltd.) in 86 g of isopropanol at this was added, and the complex alkoxide solution which consists of silicon and titanium was prepared. Next, the ammonia nature alcohol solution which changes from the methanol 300g and 75 g of ammonia solutions (25 % of the weight of concentration) to glass reaction vessels with a content volume [with agitating blades] of 3 l. was put in, and the reaction vessel was prepared. Keeping the temperature of a reaction vessel at 40 **, the liquid which melted 0.2 g of tetraethoxysilanes (the Kanto Kagaku make, 99.9% of purity) in the methanol 5g was added, it stirred for 30 minutes, and the nuclear particle was made to generate. Subsequently, the liquid which added 150 g of ammonia solutions (25 % of the weight of concentration) to 600 g of isopropanol was added to the reaction vessel, and reaction mixture was prepared. It was dropped having covered the complex alkoxide solution which consists of silicon prepared previously and titanium over the reaction vessel for about 4 hours keeping the temperature of a reaction vessel at 40 **. After the end of dropping, and also after continuing churning for 30 minutes, the tetraethyl silicate 20.0g was dropped at the reaction vessel in 30 minutes. After the end of dropping, and also after stirring for 1 hour, the solvent was removed by the evaporator, temporary quenching was carried out at 1050 ** for 2 hours, and silica covering inorganic matter compound oxide particles (J-2) were obtained.
[0052]Silica covering inorganic matter compound oxide particles (J-2) had spherical shape, and 3 nm and the surface-water-of-aggregate acid radical density of the thickness of the mean particle diameter of 0.2 micrometer, the refractive index 1.541, and the silica enveloping layer by which brewing twist presumption is carried out were the 7.2×10^{-6} equivalent / m^2.
[0053]Next, the cured body (B) which contains silica covering inorganic matter compound oxide particles (J-2) like Example 1 was produced. Cured bodies (B) were 50 % of the weight of filler content, 88% (589 nm) of light transmittance, Tg132 **, a coefficient of thermal expansion of 30 ppm/**, and 0.83% of water absorption.
[0054]167.5 g of example 3 tetramethyl silicate (trade name: the methylsilicate 39, made in Japanese Col Coat) was melted in the methanol 100g. After adding 14.0 g of chloride (0.036 % of the weight of concentration) in this liquid, it stirred for about 10 minutes. The solution which melted 88.5 g of titaniumtetrabutoxide (made by Nippon Soda Co., Ltd.) in 156 g of isopropanol at this was added, and the solution of the complex alkoxide which consists of silicon and titanium was prepared. Next, the ammonia nature alcohol solution which changes from the methanol 300g and 66 g of ammonia solutions (25 % of the weight of concentration) to glass reaction vessels with a content volume [with agitating blades] of 3 l. was put in, and the reaction vessel was prepared. Keeping the temperature of a reaction vessel at 40 **, the liquid which melted 0.2 g of tetraethoxysilanes (the Kanto Kagaku make, 99.9% of purity) in the methanol 5g was added, it stirred for 30 minutes, and the nuclear particle was made to generate. Subsequently, the liquid which added 159 g of ammonia solutions (25 % of the weight of concentration) to 600 g of isopropanol was added to the reaction vessel, and reaction mixture was prepared. It was dropped having covered the solution of the complex alkoxide which consists of silicon prepared previously and titanium over the reaction vessel for about 6 hours keeping the temperature of a reaction vessel at 40 **. After the end of dropping, and also after continuing churning for 30 minutes, it was dropped having covered the tetraethyl silicate 133g over the reaction vessel for 60 minutes. After the end of dropping, and also after stirring for 1 hour, the solvent was removed by the evaporator, temporary quenching was carried out at 1050 ** for 2 hours, and silica covering inorganic matter compound oxide particles (J-3) were obtained.
[0055]Silica covering inorganic matter compound oxide particles (J-3) had spherical shape, and 12 nm and the surface-water-of-aggregate acid radical density of the thickness of the mean particle diameter of 0.2 micrometer, the refractive index 1.540, and the silica enveloping layer by which brewing twist presumption is carried out were the 7.0×10^{-6} equivalent / m^2.
[0056]The cured bodies (C) containing the silica covering inorganic matter compound oxide particles (J-3)

prepared like Example 1 were 50 % of the weight of filler content, 50% (589 nm) of light transmittance, Tg132 **, a coefficient of thermal expansion of 30 ppm/**, and 1.03% of water absorption.
[0057]794.5 g of example 4 tetramethyl silicate (trade name: the methylsilicate 39, made in Japanese Col Coat) was melted in the methanol 300g. After adding 42.1 g of chloride (0.036 % of the weight of concentration) in this solution, it stirred for about 10 minutes. The solution which melted 265.5 g of titaniumtetrabutoxide (made by Nippon Soda Co., Ltd.) in 470 g of isopropanol at this was added, and the solution of the complex alkoxide which consists of silicon and titanium was prepared. Next, the ammonia nature alcohol solution which changes from the methanol 150g and 30.7 g of ammonia solutions (25 % of the weight of concentration) to glass reaction vessels with a content volume [with agitating blades] of 3 l. was put in, and the reaction vessel was prepared. Keeping the temperature of a reaction vessel at 40 **, the liquid which melted 0.2 g of tetraethoxysilanes (the Kanto Kagaku make, 99.9% of purity) in the methanol 5g was added, it stirred for 30 minutes, and the nuclear particle was made to generate. Subsequently, the liquid which added 81.8 g of ammonia solutions (25 % of the weight of concentration) to 300 g of isopropanol was added to the reaction vessel, and reaction mixture was prepared. It was dropped having covered the solution of the complex alkoxide which consists of silicon prepared previously and titanium over the reaction vessel for about 8 hours keeping the temperature of a reaction vessel at 40 **. After the end of dropping, and also after stirring for 1 hour, the solvent was removed by the evaporator, temporary quenching was carried out at 1050 ** for 2 hours, and inorganic compound oxide particles (J-4) were obtained. The shape of inorganic compound oxide particles (J-4) was spherical, and was inorganic powder which does not cover the silica of the mean-particle-diameter [of 0.4 micrometer], refractive-index 1.541, and surface-water-of-aggregate acid radical density 7.5×10^{-6} equivalent / m^2.
[0058]The cured bodies (D) containing the inorganic compound oxide particles (J-4) prepared like Example 1 were 60 % of the weight of filler content, 81% (589 nm) of light transmittance, Tg135 **, a coefficient of thermal expansion of 26 ppm/**, and 0.88% of water absorption.
[0059]Example Particles were compounded by the same method as Example 2 except having changed the quantitative ratio with 5 tetramethyl silicate, titaniumtetrabutoxide, and silicontetraethoxide. Temporary quenching of this was carried out at 1050 ** for 2 hours, and silica covering inorganic matter compound oxide particles (J-5) were obtained.
[0060]Silica covering inorganic matter compound oxide particles (J-5) had spherical shape, and the thickness of the mean particle diameter of 0.2 micrometer, the refractive index 1.543, and the silica enveloping layer by which brewing twist presumption is carried out was 3 nm, and the surface-water-of-aggregate acid radical density 7.0×10^{-6} equivalent / m^2.
[0061]The cured bodies (E) containing the inorganic compound oxide particles (J-5) prepared like Example 1 were 50 % of the weight of filler content, 85% (589 nm) of light transmittance, Tg134 **, a coefficient of thermal expansion of 30 ppm/**, and 0.82% of water absorption.
[0062]Example Particles were compounded by the same method as Example 2 except having changed the quantitative ratio with 6 tetramethyl silicate, titaniumtetrabutoxide, and silicontetraethoxide. Temporary quenching of this was carried out at 1050 ** for 2 hours, and silica covering inorganic matter compound oxide particles (J-6) were obtained.
[0063]Silica covering inorganic matter compound oxide particles (J-6) had spherical shape, and the thickness of the mean particle diameter of 0.2 micrometer, the refractive index 1.549, and the silica enveloping layer by which brewing twist presumption is carried out was 3 nm, and the surface-water-of-aggregate acid radical density 7.2×10^{-6} equivalent / m^2.
[0064]The cured bodies (F) containing the inorganic compound oxide particles (J-6) prepared like Example 1 were 50 % of the weight of filler content, 72% (589 nm) of light transmittance, Tg135 **, a coefficient of thermal expansion of 30 ppm/**, and 0.85% of water absorption.
[0065]61.5 g of comparative example 1 tetraethyl silicate (trade name: the ethyl silicate 28, made in Col Coat) was melted in 160 ml of methanol. After adding 1.7 ml of chloride (0.036 % of the weight of concentration) in this liquid, it held at 35 ** for 1 hour. The solution which melted 15.0 g of titaniumtetrabutoxide (made by Nippon Soda Co., Ltd.) in 100 ml of isopropanol at this was added, and the solution of the complex alkoxide which consists of silicon and titanium was prepared. Next, the ammonia nature alcohol solution which comprises 700 ml of methanol, 500 ml of normal butanol, and a 250-ml ammonia solution (25 % of the weight of concentration) was put in, and the reaction vessel was prepared. It was dropped having covered the solution of the complex alkoxide which consists of silicon prepared previously and titanium over the reaction vessel for about 4 hours

keeping the temperature of a reaction vessel at 35 **. Reaction mixture became opalescence in about 30 minutes after the dropping start. After the end of dropping, and also after stirring for 1 hour, the solvent was removed by the evaporator and the inorganic compound oxide particles (H-1) which carry out temporary quenching at 850 ** for 1 hour, and do not cover silica were obtained. The shape of the obtained particles was spherical and the mean particle diameter of 0.08 micrometer, the refractive index 1.541, and surface-water-of-aggregate acid radical density were the 10.7×10^{-6} equivalent / m^2.
[0066]The cured body (E) was prepared like Example 1 using inorganic compound oxide particles (H-1). Cured bodies (E) were Tg100 **, a coefficient of thermal expansion of 28 ppm/**, and 2.15% of water absorption 56 % of the weight of filler content, 29% (450 nm) of light transmittance, and 84% (589 nm).
[0067]132.3 g of comparative example 2 tetramethyl silicate (trade name: the methylsilicate 39, made in Japanese Col Coat) was melted in the methanol 50g. After adding 7.0 g of chloride (0.036 % of the weight of concentration) in this solution, it stirred for about 10 minutes. The solution which melted 44.3 g of titaniumtetrabutoxide (made by Nippon Soda Co., Ltd.) in 78 g of isopropanol at this was added, and the complex alkoxide solution which consists of silicon and titanium was prepared. Next, the ammonia nature alcohol solution which changes from the methanol 300g and 75 g of ammonia solutions (25 % of the weight of concentration) to glass reaction vessels with a content volume [with agitating blades] of 3 l. was put in, and the reaction vessel was prepared. Keeping the temperature of a reaction vessel at 40 **, the liquid which melted 0.2 g of tetraethoxysilanes (the Kanto Kagaku make, 99.9% of purity) in the methanol 5g was added, it stirred for 30 minutes, and the nuclear particle was made to generate. Subsequently, the liquid which added 150 g of ammonia solutions (25 % of the weight of concentration) to 600 g of isopropanol was added to the reaction vessel, and reaction mixture was prepared. It was dropped having covered the complex alkoxide solution which consists of silicon prepared previously and titanium over the reaction vessel for about 4 hours keeping the temperature of a reaction vessel at 40 **. Stirring was continued for 40 minutes after the end of dropping, and particles were obtained. Temporary quenching of the obtained particles was carried out at 850 ** for 1 hour, and inorganic compound oxide particles (H-2) were obtained.
[0068]The shape of inorganic compound oxide particles (H-2) was spherical, and the mean particle diameter of 0.2 micrometer, the refractive index 1.542, and surface-water-of-aggregate acid radical density were the 10.7×10^{-6} equivalent / m^2.
[0069]The cured body (F) which contains inorganic compound oxide particles (H-2) 50% of the weight was prepared like Example 1. This was 50 % of the weight of filler content, 86% (589 nm) of light transmittance, Tg112 **, a coefficient of thermal expansion of 30 ppm/**, and 1.84% of water absorption.
[0070]After compounding particles by the same method as comparative example 3 Example 2, temporary quenching was carried out at 800 ** for 1 hour, and inorganic compound oxide particles (H-3) were obtained.
[0071]The above-mentioned inorganic compound-oxide-particles (H-3) shape was spherical, the mean particle diameter of 0.2 micrometer, the refractive index 1.539, and surface-water-of-aggregate acid radical density were $11.0 \times 10^{-6}/m^2$, and the thickness of the silica enveloping layer by which brewing twist presumption is carried out was 3 nm.
[0072]The cured bodies (G) which contain the inorganic compound oxide particles (H-3) prepared like Example 1 50% of the weight were 50 % of the weight of filler content, 80% (589 nm) of light transmittance, Tg115 **, a coefficient of thermal expansion of 30 ppm/**, and 1.77% of water absorption.
[0073]So that the titania content in the silica titania particles to generate may be 10.6-mol% in the comparative example 4 comparative example 2, Except having changed the quantitative ratio of the used tetramethyl silicate and titaniumtetrabutoxide, particles were obtained like the comparative example 2, temporary quenching was carried out at 850 ** for 1 hour, and inorganic compound oxide particles (H-4) were obtained.
[0074]The shape of inorganic compound oxide particles (H-4) was spherical, and the mean particle diameter of 0.2 micrometer, the refractive index 1.515, and surface-water-of-aggregate acid radical density were the 10.7×10^{-6} equivalent / m^2.
[0075]The cured body (H) which contains inorganic compound oxide particles (H-4) 50% of the weight was prepared like Example 1. This was 50 % of the weight of filler content, 10% (589 nm) of light transmittance, Tg112 **, a coefficient of thermal expansion of 30 ppm/**, and 1.84% of water absorption.

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(54)【発明の名称】 エポキシ樹脂組成物

(57)【要約】
【構成】 表面水酸基密度が９×１０$^{-6}$当量／m^{2}以下である無機複合酸化物粒子とエポキシ樹脂を含有してなり、且つ無機複合酸化物粒子の屈折率（N^F_D）とエポキシ樹脂の硬化体の屈折率（N^P_D）が次式を満足することを特徴とするエポキシ樹脂組成物。
$|N^F_D - N^P_D| \leqq 0.010$。
【効果】 従来の屈折率を調整したシリカ系複合酸化物粒子とエポキシ樹脂とからなる複合樹脂（透明封止材）は、その硬化体の吸水率が高い（耐湿性が低い）、ガラス転移温度が低い、硬化時に黄変するという問題点があったが、本発明では、表面水酸基密度の低減更には粒子の表面へのシリカ層の被覆により、上記問題点を解決した。従って、従来の無機充填材を含む透明封止材に比べて優れた物性を有するので、透明封止材の信頼性が大幅に向上した。

【特許請求の範囲】

【請求項1】 表面水酸基密度が９×１０$^{-6}$当量／m^{2}以下である無機複合酸化物粒子とエポキシ樹脂を含有してなり、且つ無機複合酸化物粒子の屈折率（N^F_D）とエポキシ樹脂の硬化体の屈折率（N^P_D）が次式を満足することを特徴とするエポキシ樹脂組成物。

$|N^F_D - N^P_D| \leqq 0.010$

【請求項2】 無機複合酸化物粒子が、シリカで無機複合酸化物粒子表面を被覆したシリカ被覆無機複合酸化物粒子である請求項１記載のエポキシ樹脂組成物。

【請求項3】 請求項１記載のエポキシ樹脂組成物を硬化してなり、５８９ｎｍの光の透過率が５０％以上であることを特徴とする透明性硬化体。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は発光素子や受光素子などの光半導体を外界より保護するための透明封止材に関するものである。詳しくは、無機複合酸化物とエポキシ樹脂とよりなるエポキシ樹脂組成物及びその硬化体に関する。

【０００２】

【従来の技術】従来より、エポキシ樹脂は、機械的性質、電気的絶縁性に優れ、接着性が高く、しかも、硬化時の収縮が少ない等の特徴を有するため、半導体封止材として広く使用されてきた。しかし、回路の高集積化に伴い、耐湿性、耐熱性などの高物性が求められるようになった。そこで、エポキシ樹脂の耐熱性や耐湿性の物性の向上を図るため、一般に、アルミナやシリカ等の無機充填材の添加が行われてきた。例えば、特開平２－２６３１３号、特開平２－１４５４１５号、特開平２－１４５４１６号、特開平２－１５８６３７号には、球状シリカを充填することによって、低熱膨張係数、高耐湿性の封止材用樹脂組成物が得られることが開示されている。

【０００３】

【発明が解決しようとする課題】一方、近年では、オプトエレクトロニクス関連技術の進歩が著しく、光半導体の封止には、上記物性に加えて透明性が求めれるようになった。しかし、上記の無機充填材を複合化したエポキシ樹脂の硬化体は、透明性がほとんどなく、光半導体の封止材には適さない。

【０００４】透明封止材として無機充填材を含有しないエポキシ樹脂組成物が種々提案されている。しかし、熱膨張係数が高く、耐熱性、耐湿性の問題点も解決されていないため、無機充填材を含む透明封止材の開発が望まれている。

【０００５】これに応えるものとして、特定の屈折率を有する無機充填材を用いたエポキシ樹脂組成物が提案されている。このような充填材としては、シリカをベースとする複合金属酸化物が用いられるが、この場合、充填材を添加したのにもかかわらず、硬化体の耐湿性やガラス転移温度が十分でなく素子と封止材間の剥離やパッケージクラックの問題が残されていた。又、硬化時に黄変するため光透過率が低下するという問題点があった。

【０００６】

【課題を解決するための手段】本発明者らは、無機充填材を含む透明封止材について上記課題を解決すべく鋭意検討した結果、無機充填材の表面水酸基密度を減らすこと更には無機充填材の表面をシリカで被覆することによって、硬化体の耐湿性及びガラス転移温度が向上し、更に硬化時の黄変が低減することを見いだし、本発明を完成するに至った。

【０００７】即ち、本発明は、表面水酸基密度が９×１０$^{-6}$当量／m^{2}以下である無機複合酸化物粒子とエポキシ樹脂を含有してなり、且つ無機複合酸化物粒子の屈折率（N^F_D）とエポキシ樹脂の硬化体の屈折率（N^P_D）が次式を満足することを特徴とするエポキシ樹脂組成物である。

【０００８】$|N^F_D - N^P_D| \leqq 0.010$

他の発明は、該エポキシ樹脂組成物を硬化してなり、５８９ｎｍの光の透過率が５０％以上であることを特徴とする透明性硬化体である。

【０００９】本発明の無機複合酸化物粒子は、表面水酸基密度の調整後の屈折率（N^F_D）が上記式を満たすものであれば、公知の無機複合酸化物粒子又はガラス微粒子が特に限定されることなく採用される。該粒子の屈折率は、最終的に得られる無機複合酸化物粒子を含有するエポキシ樹脂組成物の硬化体が透明性を保持するために、後述するエポキシ樹脂硬化体のそれに併せて上記範囲内に納める必要がある。無機複合酸化物粒子の組成は、目的とする屈折率が得られるものであれば特に制限されない。特に好適な無機複合酸化物粒子の成分として、シリカを一成分とする複合酸化物が挙げられる。特に好適な複合酸化物を例示すれば、シリカ及びシリカと複合化（結合）可能な周期律表第２族、第３族、及び第４族よりなる群から選ばれた少なくとも一種の金属酸化物よりなる複合酸化物である。上記金属酸化物を具体的に例示すれば、酸化マグネシウム、酸化カルシウム、酸化ストロンチウム、酸化バリウム、酸化ホウ素、酸化アルミニウム、酸化チタン、酸化ジルコニウム、酸化ハフニウム、酸化錫、酸化亜鉛等が代表的である。これらの複合酸化物は、シリカのシリコンと酸素を介して結合する。上記複合酸化物におけるシリカの割合は、特に制限されるものではないが、特に、６０～９９モル％、好ましくは、８０～９５モル％のものが本発明の目的を達成する上で好適である。

【００１０】又、本発明の無機複合酸化物粒子の屈折率の調整は、シリカと複合する金属酸化物の種類、及び、比率を変えることにより行なうことが一般的である。この場合、特に、酸化ストロンチウム、酸化チタニウム、酸化ジルコニウム、酸化ハフニウム、酸化錫等のシリカ

よりも屈折率が高い酸化物を用いることが好ましい。上記無機複合酸化物粒子の製造方法は、公知の方法が特に制限なく採用される。例えば、ゾルーゲル法、粉砕－分級法、共沈法等がある。特に代表的な製造方法を例示すれば、部分的に加水分解されたアルコキシシランとチタン又はジルコニウム等の金属のアルコキシドとを混合した後、該混合溶液をアルカリ性のアルコール溶液に攪拌しながら滴下するゾルーゲル法がある。この場合、出発物質の量比を調節することにより、得られる無機粉末の屈折率を調節することができる。

【００１１】表面水酸基密度が９×１０$^{-6}$当量／m^{2}以下である無機複合酸化物粒子は、上述の無機複合酸化物粒子表面の水酸基の量を調整したものである。無機複合酸化物粒子の表面水酸基密度が９×１０$^{-6}$当量／m^{2}を越える場合には、エポキシ樹脂に混入後硬化して得られるエポキシ樹脂組成物硬化体の耐湿性が悪く、又ガラス転移温度が向上しない。表面水酸基密度は小さいほど好ましいが、次ぎに述べる粒子の焼結性及び結晶性ひいては硬化体の透明性に影響を及ぼす粒子の加熱温度との兼ね合いで現時点では、６×１０$^{-6}$当量／m^{2}程度のものまで得ることができる。

【００１２】表面の水酸基密度を低減させるには公知の方法を制限なく採用できる。例えば、代表的な方法として加熱処理する方法がある。加熱温度は、無機複合酸化物粒子が結晶化しない、及び粒子同士が焼結しない範囲であれば任意に選択することができる。温度が高すぎると、無機複合酸化物粒子が結晶化したり焼結するため、エポキシ樹脂組成物硬化体の透明性が低下する。また、加熱温度が低すぎると、無機複合酸化物粒子の表面水酸基密度を下げることができない。そこで、加熱温度は、９００～１２００℃が好ましく、９５０～１１００℃がより好ましい。加熱に要する時間は、無機複合酸化物粒子が結晶化しない範囲であれば任意に選択できる。

【００１３】本発明において、無機複合酸化物粒子の平均粒子径は、特に限定されるものではないが、エポキシ樹脂組成物硬化体の透明性の指標となる光透過率は、平均粒子径が小さいほど高い。このため、平均粒子径は２０μm以下が好ましく、０．０４～５μmがより好ましい。更に、上記無機粒子は、平均粒子径が異なる二種以上のものを混合して使用してもよい。上述の通り、平均粒子径が小さいほど硬化したエポキシ樹脂組成物の透明性は高く、平均粒子径が大きくなると硬化体の透明性に温度依存性がでてくるので、発熱などを伴う箇所で用いる場合には、平均粒子径が小さいものを用いるのが好ましい。

【００１４】また、無機複合酸化物粒子の形状は特に制限されるものではないが、エポキシ樹脂と混合した場合に流動性に優れた組成物を得る為には、球状であることが好ましい。

【００１５】無機複合酸化物粒子の表面をシリカで被覆したシリカ被覆無機複合酸化物粒子の製造方法には、公知の方法を制限なく採用できる。例えば、無機複合金属酸化物粒子をアルカリ性アルコール溶液に分散させた液に、テトラエチルシリケートを滴下し、テトラエチルシリケートの加水分解物を無機複合酸化物粒子の表面に析出させる方法がある。シリカ被覆無機複合酸化物粒子のシリカ被覆層の厚さは、該シリカ被覆無機複合酸化物粒子とエポキシ樹脂とよりなるエポキシ樹脂組成物の硬化体の透明性が低下しない範囲であれば任意に選択できる。この厚さとして、例えば、１～３０nmが好ましく３～１５nmがより好ましい。被覆層の厚さの調整は、被覆に用いるシリカの原料の量と無機複合酸化物粒子の比表面積との比を調整することによって行われる。またその厚さの測定は、仕込組成比から計算によって求めることもできるが、組成によっては透過型電子顕微鏡写真の観察によって行われる。透過型電子顕微鏡観察用の試料は、例えば、本発明のシリカ被覆無機複合酸化物粒子をアクリレート又はエポキシ等の樹脂に包埋した後、研磨し粒子の断面を観察することができる。

【００１６】以上のようにして得られたシリカ被覆無機複合酸化物粒子は、粒子に含まれる水分、有機物等を除去し、且つ表面水酸基密度を９×１０$^{-5}$当量／m^{2}以下に調製するために加熱（仮焼）する。仮焼温度は、特に限定されるものではないが、粒子同士の焼結などを考慮すると、９００～１２００℃が好ましく、９５０～１１００℃がより好ましい。また、仮焼時間は特に限定されるものではないが、３０分～１０時間が好ましい。

【００１７】一般に、平均粒子径が１μm以下の複合酸化物微粒子を１０００℃以上の高温で熱処理すると、粒子同士が焼結し粒子の単分散性が低下する傾向にある。本発明のシリカ被覆無機複合酸化物粒子のように、無機複合酸化物粒子の表面を化学的に不活性なシリカで被覆すれば、１０００℃以上の高温で熱処理しても単分散性が優れたものが得られる。

【００１８】本発明のシリカ被覆無機複合酸化物微粒子の屈折率（N^F_D）も前記エポキシ樹脂硬化体の屈折率（N^P_D）との関係式を満たす必要がある。無機複合酸化物粒子にシリカを被覆すると、シリカ被覆層の厚さに応じて、シリカ被覆無機複合酸化物粒子の屈折率が低下する。そのため、無機複合酸化物粒子の屈折率は、予め目標とする屈折率よりも高めに設定しておくのが好ましい。

【００１９】尚、屈折率の測定は、後記するように、液浸法によりアッベ屈折計を使用して行うことができる。

【００２０】本発明で用いる表面水酸基密度が９×１０$^{-5}$当量／m^{2}以下である無機複合酸化物粒子は、粒子の性状の安定性を更に高めると共に、エポキシ樹脂への分散性を向上させるため、有機硅素化合物、有機チタン化合物等の処理剤により表面処理を行なうことができる。この処理は、処理剤を溶解した溶媒と無機複合酸化物粒

子とを接触させた後、該溶媒を除去するのが一般的である。処理剤の有機硅素化合物としては、γ－グリシドキシプロピルトリメトキシシラン、γ－メタクリロキシプロピルトリメトキシシラン、ビニルトリエトキシシラン等のアルコキシシラン化合物が好適であり、中でもエポキシ基を有するものが特に好適である。上記表面処理の後、複合酸化物粒子が凝集している場合には、水、アルコール、アセトン等の溶液に分散させた後、超音波をかけることによって、或は、擂潰機などによって、粒子の凝集を解くのが好ましい。

【0021】以上のように調製された無機複合酸化物粒子は、エポキシ樹脂と混練しエポキシ樹脂組成物が調製される。

【0022】本発明で使用されるエポキシ樹脂として、公知のものが特に制限なく採用される。例えば、ビスフェノールA型エポキシ樹脂、フェノールノボラック型エポキシ樹脂、脂環式エポキシ樹脂、複素環型エポキシ樹脂、グリシジルエステル型エポキシ樹脂、グリシジルアミン型エポキシ樹脂、ハロゲン化エポキシ樹脂等のエポキシ樹脂成分を主要成分とし、これに必要に応じて硬化剤、希釈剤、可塑性付与剤、難燃剤、紫外線吸収剤、顔料等を配合したものが挙げられる。

【0023】上記硬化剤は、エポキシ樹脂の重合及び架橋を進めるもので、公知のものが特に制限なく使用される。例えば、テトラヒドロ無水フタル酸、無水フタル酸、無水ピロメリット酸、無水メチルナジック酸などの酸無水物が挙げられる。上記硬化剤の配合量は、公知の範囲が特に制限なく採用される。一般には、前記エポキシ樹脂成分のエポキシ基1当量に対してカルボキシル基換算で0.5～1.5当量の範囲となるように硬化剤を使用することが好ましい。

【0024】又、硬化促進剤も公知のものが特に制限なく使用される。例えば、2－メチルイミダゾール、2、4－ジヒドラジノ－6－メチルアミノ－S－トリアジン、2－エチル－4－メチルイミダゾール等のイミダゾール化合物、フッ化ホウ素、オニウム塩等が挙げられる。これらの硬化促進剤は、必要に応じて一種、又は二種以上が使用される。上記硬化促進剤の配合量は、公知の範囲が特に制限なく採用される。一般には、前記エポキシ樹脂成分と硬化剤の合計量に対して0．1～8重量%使用することが好ましい。

【0025】又、希釈剤は、エポキシ樹脂が高粘度の場合、作業性、脱泡性、充填材の濡れ等を向上するために添加されるものであり、公知のものが特に制限なく使用される。例えば、オレフィンオキシド、オクチレンオキサイド、スチレンオキサイド等のモノエポキシ反応性希釈剤、ブタジエンジオキサイド、ジメチレンペンタンジオキサイド、ジエチレングリコールジグリシジルエーテル等のポリエポキシ反応性希釈剤等が挙げられる。上記希釈剤の配合量は、公知の範囲が特に制限なく採用される。一般には、前記エポキシ樹脂成分に対して1～50重量%で使用される。

【0026】更に、難燃剤も公知のものが特に制限なく使用される。例えば、テトラブロモビスフェノールA、トリス（2、3－ジブロモプロピル）ホスフェート、トリクレジルフォスフェート等が挙げられる。上記難燃剤の配合量は、公知の範囲の中から本発明の効果に影響を与えない範囲で添加すればよい。

【0027】本発明において、エポキシ樹脂組成物中の無機複合酸化物粒子の割合は、20～90重量%、好ましくは、30～80重量%である。無機粒子の割合が、20重量%未満の場合は、エポキシ樹脂組成物の硬化体の耐湿性、耐熱性等が十分ではなく、また、この割合が90重量%を越える場合には、エポキシ樹脂組成物の流動性、及び取扱性が低下する。

【0028】本発明において、無機複合酸化物粒子とエポキシ樹脂との混合方法は特に限定されず、公知の方法が制限なく採用される。例えば、室温または加熱下に、自動擂潰機、ニーダー、乳鉢、アトライタ、ローラー、押し出し機等を使用してシェアをかけながら混練する方法が好適である。

【0029】本発明のエポキシ樹脂組成物は、無機複合酸化物粒子及びエポキシ樹脂を主成分とするため、硬化前には一般にペースト状、粉末状、又は固形状である。即ち、室温で液状のエポキシ樹脂を使用した場合には、得られる樹脂組成物が一般にペースト状であり、又、室温でペースト状又は固形状のエポキシ樹脂を用いた場合には、得られる樹脂組成物が粉末状、顆粒状、又は、固形状である。

【0030】本発明のエポキシ樹脂組成物において、酸化物粒子がエポキシ樹脂中に凝集状態で存在する場合は、得られる硬化体の透明性の低下を招くことがある。そのため、組成物中の凝集粒子は、上記混合方法等により、できるだけ凝集を解くことが好ましい。又、エポキシ樹脂組成物の硬化体中に存在する気泡も樹脂の透明性を低下させる原因となるので、気泡を除去することが好ましい。

【0031】本発明のエポキシ樹脂組成物は、通常の方法により硬化させうる。特に好適な硬化条件を例示すれば、加圧下、又は、常圧下に80～150℃の温度で2～30時間加熱する方法が挙げれれる。

【0032】本発明の透明性硬化体は、波長589nmの光透過率が50%以上である。光透過率は、実施例で記述するように、厚さ1㎜の板状材料について波長589nmの光の透過率を測定した値である。尚、上記値は、硬化体が顔料を含み、且つ該顔料の吸収波長が上記589nmの波長を含む場合は、該吸収による数値を補正した値をいう。

【0033】従来の無機複合酸化物を用いたエポキシ樹脂組成物では、特願平2－415291に記載されてい

るように、無機複合酸化物粒子とエポキシ樹脂の硬化体の屈折率は、特定の範囲内で屈折率差を有する場合が最も透明であった。この理由として、無機複合酸化物粒子とエポキシ樹脂との界面に低屈折率層を生じ、この低屈折率層が無機複合酸化物粒子とエポキシ樹脂との屈折率差を中和すると推定していた。　しかし、本発明のエポキシ樹脂組成物では、表面水酸基密度が9×10^{-6}当量／m^2以下である無機複合酸化物粒子とエポキシ樹脂との屈折率の値が近い程、硬化体が高い透明性を示す。この原因として、以下のように推察される。即ち、本発明のエポキシ樹脂組成物では、用いる粒子の表面が、特願平２－４１５２９１の粒子に比べて不活性であるため、粒子とエポキシ樹脂との界面に生じる低屈折率層が減少、或は、消滅したためと考えれれる。

【００３４】本発明の硬化体は、含有される気泡の量、凝集粒子の量が、少ないほど好ましい。

【００３５】

【発明の効果】従来の屈折率が調整されたシリカ系複合酸化物粒子とエポキシ樹脂とからなる複合樹脂（透明封止材）は、その硬化体の吸水率が高い即ち耐湿性が低い、ガラス転移温度が低い、硬化時に黄変するという問題点があったが、本発明では、表面水酸基密度の低減更には粒子の表面へのシリカ層の被覆により、上記問題点を解決した。

【００３６】硬化体の耐湿性が向上したのは、表面水酸基密度を低減させることによって硬化体が水分を取り込みにくくなったためと考えられる。

【００３７】また、ガラス転移温度の向上の原因は、明かではないが次のように推察される。従来は、無機粒子とエポキシ樹脂とを混練する際、無機粒子の表面の水酸基がエポキシ樹脂と反応し、エポキシ樹脂組成物の粘度が局部的に上昇し、エポキシ樹脂の硬化反応が十分に進行しなかった。ところが、表面の水酸基密度を低減させることによって、界面での反応が少なくなり硬化反応がより均一に進行するようになった。或は、エポキシ樹脂組成物中の複合酸化物粒子の表面に非常に小さい孔又は凹凸面が存在する。この凹凸は、エポキシ樹脂組成物中で空隙を生じ易く、そのボイドがエポキシ樹脂組成物のガラス転移温度を下げていた。しかし、表面の水酸基密度を下げること更には粒子表面をシリカで被覆することによって無機粒子の表面が滑らかになり、該ボイドが減少しガラス転移温度が向上した。硬化体の黄変が少なくなった原因も明確ではないが、次のように考えられる。従来の複合酸化物粒子では、表面が活性なため何等かの触媒作用を起こし、硬化反応時に樹脂の一部が酸化されたものと考えられる。複合酸化物粒子の表面は、シリカで被覆されたことによって、複合酸化物粒子表面が不活性になり、以前のような樹脂の酸化反応が起こりにくくなったと考えられる。

【００３８】以上のように、本発明の透明性硬化体は、従来の無機充填材を含む透明封止材に比べて優れた物性を有するので、透明封止材の信頼性が大幅に向上した。

【００３９】

【実施例】以下、実施例により本発明を具体的に説明するが、本発明は、これらの実施例に限定されるものではない。尚、実施例及び比較例に於て、各種測定は、下記の方法により行なった。

【００４０】（１）平均粒子径（平均粒径）
粒子をアンモニア性メタノール中に分散させた後、粒度分布計（大塚電子製）で粒子径分布を測定した。

【００４１】（２）粒子の屈折率
試料を屈折率が異なる液に懸濁させ、懸濁液が透明に見えるときの液の屈折率をアッベの屈折計によって測定した。

【００４２】（３）粒子の表面水酸基密度
無機複合酸化物粒子を３００℃で３時間加熱し、吸着水を除去した。この時の粒子の重量をW_1とする。その後、更に１０００℃で１時間加熱すると、無機複合酸化物粒子より水の脱離反応が起こり、粒子の重量はW_2になった。W_1及びW_2の測定は、加熱炉付きカールフィシャー水分測定装置（三菱化成工業社製、ＣＡ－０２）で行った。以上得られたW_1，W_2、及び、比表面積（Ｓｇ）の値より、単位面積当りの水酸基密度（10^{-6}当量／m^2）を求めた。

【００４３】（４）粒子の比表面積
粒子の表面水酸基密度を求めるのに必要な無機複合酸化物粒子の比表面積Ｓｇ（m^2／ｇ）は、ＢＥＴ比表面積計（島津製作所製、フローソーブ２１００）により求めた。

【００４４】（５）硬化体の光透過率
２枚のガラス板間の距離をスペーサで４ｍｍに調整したモールドに、硬化前エポキシ樹脂組成物を填入し、１００℃で２時間、更に１５５℃で３時間加熱し、ガラス板に挟まれた厚さ４ｍｍで板状のエポキシ樹脂組成物の硬化体を得た。この硬化体の光透過率を、ガラス板から外すことなく、分光光度計（日立製作所製，Ｕ－３２１０）で測定した。ベースラインは、２枚のガラス板の光透過率より補正した。

【００４５】（６）硬化体のガラス転移温度（Ｔｇ）及び線膨張係数
長さ２０ｍｍ、直径４ｍｍの円柱状硬化体を作製し、熱機械測定装置（リガク電機製、Ｔｈｅｒｍｏｆｌｅｘ）により、昇温速度４℃／ｍｉｎ、測定温度範囲：室温～２００℃での測定結果より、線膨張係数を求めた。ガラス転移温度（Ｔｇ）は、試料の単位温度当りの膨張の屈曲点を示す温度とした。

【００４６】（７）煮沸吸水率（吸水率）
３０×１５×４ｍｍの硬化体を試験片とし、煮沸水中で２０時間保存した。煮沸水中保存前後の重量より、下記式によって求めた。

【0047】
【数1】$A=\{(W_b-W_a)/W_a\}\times 100$
A：煮沸吸水率（％）
Wa：煮沸水中に保存前の試験片の重量（g）
Wb：煮沸水中に保存後の試験片の重量（g）
実施例１
テトラエチルシリケート（商品名：エチルシリケート２８、コルコート（株）製）３０．６gをメタノール１２０mlに溶かした。この溶液に塩酸（濃度０．０３６重量％）１．３mlを添加した後、３５℃に１時間保持した。これにチタンテトラブトキシド（日本曹達社製）１５．０gをイソプロパノール１００mlに溶かした溶液を添加し、ケイ素とチタンよりなる複合アルコキサイド溶液を調製した。次に、撹拌羽根付きの内容積３リットルのガラス製反応器にメタノール７００ml、ノルマルブタノール５００ml、及び２５０mlのアンモニア水（濃度２５重量％）とから成るアンモニア性アルコール溶液を入れ、反応槽を準備した。反応槽の温度を３５℃に保ちながら、先に調製したケイ素とチタンよりなる複合アルコキシドの溶液を反応槽に約４時間かけて滴下した。滴下開始後、約３０分で反応液は、乳白色になった。滴下終了後、更に３０分間撹拌を続けた後、テトラエチルシリケート１５．２gをメタノール４０mlに溶かした溶液を、反応槽に１時間で滴下した。更に１時間反応液を撹拌した後、エバポレータで反応液の溶媒を除去し、１０００℃で１時間仮焼しシリカ被覆無機複合酸化物粒子（J－１）を得た。
【0048】シリカ被覆無機複合酸化物粒子（J－１）は、平均粒径０．０８μm、屈折率１．５３９、仕込より推定される被覆膜の厚さ７nm、表面水酸基密度８．５×10^{-6}当量／m^2であった。
【0049】次に、ビスフェノールA型エポキシ樹脂１gに無水４－メチル－ヘキサヒドロフタル酸０．８０g、及び２－メチル－４－イミダゾール４．２mg、シリカ被覆無機複合酸化物粒子（J－１）２．５gを添加し、乳鉢で約４０分間混合し、シリカ被覆無機複合酸化物粒子（J－１）を５６重量％含むペースト状のエポキシ樹脂組成物を得た。この組成物は、超音波をかけながら３０分間真空に保ち、脱泡した。次いで、所定のテフロン製モールドに注入し、加圧重合（１１０℃、１２時間）して硬化体を得た。尚、ビスフェノールA型エポキシ樹脂１gに無水４－メチル－ヘキサヒドロフタル酸０．８０g、及び２－メチル－４－イミダゾール４．２mgを混合したものの硬化体の屈折率は１．５４０であった。
【0050】得られた硬化体（A）は、充填材含有率５６重量％、光透過率５５％（４５０nm）及び８７％（５８９nm）、Tg１２０℃、熱膨張係数２８ppm／℃、吸水率１．１８％であった。
【0051】実施例２
テトラメチルシリケート（商品名：メチルシリケート３９、日本コルコート（株）製）１３０．９gをメタノール５５gに溶かした。この溶液に塩酸（濃度０．０３６重量％）７．７gを添加した後、約１０分間撹拌した。これにチタンテトラブトキシド（日本曹達社製）４８．７gをイソプロパノール８６gに溶かした溶液を添加し、ケイ素とチタンよりなる複合アルコキシド溶液を調製した。次に、撹拌羽根付きの内容積３リットルのガラス製反応槽にメタノール３００g、アンモニア水（濃度２５重量％）７５gとから成るアンモニア性アルコール溶液を入れ、反応槽を準備した。反応槽の温度を４０℃に保ちながら、テトラエトキシシラン（関東化学（株）製、純度９９．９％）０．２gをメタノール５gに溶かした液を加え、３０分間撹拌して核粒子を生成させた。次いで、イソプロパノール６００gにアンモニア水（濃度２５重量％）１５０gを加えた液を反応槽に添加して反応液を調製した。反応槽の温度を４０℃に保ちながら、先に調製したケイ素とチタンよりなる複合アルコキシド溶液を反応槽に約４時間かけて滴下した。滴下終了後、更に３０分間撹拌を続けた後、テトラエチルシリケート２０．０gを、反応槽に３０分で滴下した。滴下終了後、更に１時間撹拌した後、エバポレータで溶媒を除去し、１０５０℃で２時間仮焼しシリカ被覆無機複合酸化物粒子（J－２）を得た。
【0052】シリカ被覆無機複合酸化物粒子（J－２）は、形状が球状で、平均粒子径０．２μm、屈折率１．５４１、仕込より推定されるシリカ被覆層の厚さは３nm、表面水酸基密度は、７．２×10^{-5}当量／m^2であった。
【0053】次に、実施例１と同様にしてシリカ被覆無機複合酸化物粒子（J－２）を含む硬化体（B）を作製した。硬化体（B）は、充填材含有率５０重量％、光透過率８８％（５８９nm）、Tg１３２℃、熱膨張係数３０ppm／℃、吸水率０．８３％であった。
【0054】実施例３
テトラメチルシリケート（商品名：メチルシリケート３９、日本コルコート（株）製）１６７．５gをメタノール１００gに溶かした。この液に塩酸（濃度０．０３６重量％）１４．０gを添加した後、約１０分間撹拌した。これにチタンテトラブトキシド（日本曹達社製）８８．５gをイソプロパノール１５６gに溶かした溶液を添加し、ケイ素とチタンよりなる複合アルコキシドの溶液を調製した。次に、撹拌羽根付きの内容積３リットルのガラス製反応槽にメタノール３００g、アンモニア水（濃度２５重量％）６６gとから成るアンモニア性アルコール溶液を入れ、反応槽を準備した。反応槽の温度を４０℃に保ちながら、テトラエトキシシラン（関東化学（株）製、純度９９．９％）０．２gをメタノール５gに溶かした液を加え、３０分間撹拌して核粒子を生成させた。次いで、イソプロパノール６００gにアンモニア

水（濃度２５重量％）１５９ｇを加えた液を反応槽に添加して反応液を調製した。反応槽の温度を４０℃に保ちながら、先に調製したケイ素とチタンよりなる複合アルコキシドの溶液を反応槽に約６時間かけて滴下した。滴下終了後、更に３０分間撹拌を続けた後、テトラエチルシリケート１３３ｇを、反応槽に６０分かけて滴下した。滴下終了後、更に１時間撹拌した後、エバポレータで溶媒を除去し、１０５０℃で２時間仮焼しシリカ被覆無機複合酸化物粒子（Ｊ－３）を得た。

【００５５】シリカ被覆無機複合酸化物粒子（Ｊ－３）は、形状が球状で、平均粒子径０．２μm、屈折率１．５４０、仕込より推定されるシリカ被覆層の厚さは１２ｎｍ、表面水酸基密度は、７．０×１０$^{-5}$当量／m^{2}であった。

【００５６】実施例１と同様にして調製したシリカ被覆無機複合酸化物粒子（Ｊ－３）を含む硬化体（Ｃ）は、充填材含有率５０重量％、光透過率５０％（５８９ｎｍ）、Ｔｇ１３２℃、熱膨張係数３０ｐｐｍ／℃、吸水率１．０３％であった。

【００５７】実施例４

テトラメチルシリケート（商品名：メチルシリケート３９、日本コルコート（株）製）７９４．５ｇをメタノール３００ｇに溶かした。この溶液に塩酸（濃度０．０３６重量％）４２．１ｇを添加した後、約１０分間撹拌した。これにチタンテトラブトキシド（日本曹達社製）２６５．５ｇをイソプロパノール４７０ｇに溶かした溶液を添加し、ケイ素とチタンよりなる複合アルコキシドの溶液を調製した。次に、撹拌羽根付きの内容積３リットルのガラス製反応槽にメタノール１５０ｇ、アンモニア水（濃度２５重量％）３０．７ｇとから成るアンモニア性アルコール溶液を入れ、反応槽を準備した。反応槽の温度を４０℃に保ちながら、テトラエトキシシラン（関東化学（株）製、純度９９．９％）０．２ｇをメタノール５ｇに溶かした液を加え、３０分間撹拌して核粒子を生成させた。次いで、イソプロパノール３００ｇにアンモニア水（濃度２５重量％）８１．８ｇを加えた液を反応槽に添加して反応液を調製した。反応槽の温度を４０℃に保ちながら、先に調製したケイ素とチタンよりなる複合アルコキシドの溶液を反応槽に約８時間かけて滴下した。滴下終了後、更に１時間撹拌した後、エバポレータで溶媒を除去し、１０５０℃で２時間仮焼し無機複合酸化物粒子（Ｊ－４）を得た。無機複合酸化物粒子（Ｊ－４）の形状は球状で、平均粒子径０．４μm、屈折率１．５４１、表面水酸基密度７．５×１０$^{-5}$当量／m^{2}のシリカを被覆しない無機粉末であった。

【００５８】実施例１と同様にして調製した無機複合酸化物粒子（Ｊ－４）を含む硬化体（Ｄ）は、充填材含有率６０重量％、光透過率８１％（５８９ｎｍ）、Ｔｇ１３５℃、熱膨張係数２６ｐｐｍ／℃、吸水率０．８８％であった。

【００５９】実施例　５

テトラメチルシリケート、チタンテトラブトキシド及びシリコンテトラエトキシドとの量比を変えた以外は、実施例２と同様の方法で粒子を合成した。これを１０５０℃で２時間仮焼しシリカ被覆無機複合酸化物粒子（Ｊ－５）を得た。

【００６０】シリカ被覆無機複合酸化物粒子（Ｊ－５）は、形状が球状で、平均粒子径０．２μm、屈折率１．５４３、仕込より推定されるシリカ被覆層の厚さは３ｎｍ、表面水酸基密度７．０×１０$^{-5}$当量／m^{2}であった。

【００６１】実施例１と同様にして調製した無機複合酸化物粒子（Ｊ－５）を含む硬化体（Ｅ）は、充填材含有率５０重量％、光透過率８５％（５８９ｎｍ）、Ｔｇ１３４℃、熱膨張係数３０ｐｐｍ／℃、吸水率０．８２％であった。

【００６２】実施例　６

テトラメチルシリケート、チタンテトラブトキシド及びシリコンテトラエトキシドとの量比を変えた以外は、実施例２と同様の方法で粒子を合成した。これを１０５０℃で２時間仮焼しシリカ被覆無機複合酸化物粒子（Ｊ－６）を得た。

【００６３】シリカ被覆無機複合酸化物粒子（Ｊ－６）は、形状が球状で、平均粒子径０．２μm、屈折率１．５４９、仕込より推定されるシリカ被覆層の厚さは３ｎｍ、表面水酸基密度７．２×１０$^{-5}$当量／m^{2}であった。

【００６４】実施例１と同様にして調製した無機複合酸化物粒子（Ｊ－６）を含む硬化体（Ｆ）は、充填材含有率５０重量％、光透過率７２％（５８９ｎｍ）、Ｔｇ１３５℃、熱膨張係数３０ｐｐｍ／℃、吸水率０．８５％であった。

【００６５】比較例１

テトラエチルシリケート（商品名：エチルシリケート２８、コルコート（株）製）６１．５ｇをメタノール１６０mlに溶かした。この液に塩酸（濃度０．０３６重量％）１．７ｍｌを添加した後、３５℃に１時間保持した。これにチタンテトラブトキシド（日本曹達社製）１５．０ｇをイソプロパノール１００ｍｌに溶かした溶液を添加し、ケイ素とチタンよりなる複合アルコキシドの溶液を調製した。次に、メタノール７００ｍｌ、ノルマルブタノール５００ｍｌ、及び２５０ｍｌのアンモニア水（濃度２５重量％）とから成るアンモニア性アルコール溶液を入れ、反応槽を準備した。反応槽の温度を３５℃に保ちながら、先に調製したケイ素とチタンよりなる複合アルコキシドの溶液を反応槽に約４時間かけて滴下した。滴下開始後、約３０分で反応液は、乳白色になった。滴下終了後、更に１時間撹拌した後、エバポレータで溶媒を除去し、８５０℃で１時間、仮焼しシリカを被覆しない無機複合酸化物粒子（Ｈ－１）を得た。得られ

た粒子の形状は球状で、平均粒子径０．０８μm、屈折率１．５４１、表面水酸基密度は１０．７×１０$^{-6}$当量／m^{2}であった。

【００６６】無機複合酸化物粒子（Ｈ－１）を用い実施例１と同様にして、硬化体（Ｅ）を調製した。硬化体（Ｅ）は、充填材含有率５６重量％、光透過率２９％（４５０ｎｍ）及び８４％（５８９ｎｍ）、Ｔｇ１００℃、熱膨張係数２８ｐｐｍ／℃、吸水率２．１５％であった。

【００６７】比較例２

テトラメチルシリケート（商品名：メチルシリケート３９、日本コルコート（株）製）１３２．３ｇをメタノール５０ｇに溶かした。この溶液に塩酸（濃度０．０３６重量％）７．０ｇを添加した後、約１０分間撹拌した。これにチタンテトラブトキシド（日本曹達社製）４４．３ｇをイソプロパノール７８ｇに溶かした溶液を添加し、ケイ素とチタンよりなる複合アルコキシド溶液を調製した。次に、撹拌羽根付きの内容積３リットルのガラス製反応槽にメタノール３００ｇ、アンモニア水（濃度２５重量％）７５ｇとから成るアンモニア性アルコール溶液を入れ、反応槽を準備した。反応槽の温度を４０℃に保ちながら、テトラエトキシシラン（関東化学（株）製、純度９９．９％）０．２ｇをメタノール５ｇに溶かした液を加え、３０分間撹拌して核粒子を生成させた。次いで、イソプロパノール６００ｇにアンモニア水（濃度２５重量％）１５０ｇを加えた液を反応槽に添加して反応液を調製した。反応槽の温度を４０℃に保ちながら、先に調製したケイ素とチタンよりなる複合アルコキシド溶液を反応槽に約４時間かけて滴下した。滴下終了後、更に４０分間撹拌を続け粒子を得た。得られた粒子を８５０℃で１時間仮焼し無機複合酸化物粒子（Ｈ－２）を得た。

【００６８】無機複合酸化物粒子（Ｈ－２）の形状は球状で、平均粒子径０．２μm、屈折率１．５４２、表面＊＊水酸基密度は、１０．７×１０$^{-6}$当量／m^{2}であった。

【００６９】実施例１と同様にして、無機複合酸化物粒子（Ｈ－２）を５０重量％含む硬化体（Ｆ）を調製した。これは、充填材含有率５０重量％、光透過率８６％（５８９ｎｍ）、Ｔｇ１１２℃、熱膨張係数３０ｐｐｍ／℃、吸水率１．８４％であった。

【００７０】比較例３

実施例２と同様の方法で粒子を合成した後、８００℃で１時間仮焼し無機複合酸化物粒子（Ｈ－３）を得た。

【００７１】上記無機複合酸化物粒子（Ｈ－３）形状は球状で、平均粒径０．２μm、屈折率１．５３９、表面水酸基密度は、１１．０×１０$^{-6}$／m^{2}で、仕込より推定されるシリカ被覆層の厚さは、３ｎｍであった。

【００７２】実施例１と同様にして調製した無機複合酸化物粒子（Ｈ－３）を５０重量％含む硬化体（Ｇ）は、充填材含有率５０重量％、光透過率８０％（５８９ｎｍ）、Ｔｇ１１５℃、熱膨張係数３０ｐｐｍ／℃、吸水率１．７７％であった。

【００７３】比較例４

比較例２に於て、生成するシリカ－チタニア粒子中のチタニア含有率が１０．６モル％になるように、用いたテトラメチルシリケートとチタンテトラブトキシドとの量比を変更した以外は、比較例２と同様にして粒子を得、８５０℃で１時間仮焼し無機複合酸化物粒子（Ｈ－４）を得た。

【００７４】無機複合酸化物粒子（Ｈ－４）の形状は球状で、平均粒子径０．２μm、屈折率１．５１５、表面水酸基密度は、１０．７×１０$^{-6}$当量／m^{2}であった。

【００７５】実施例１と同様にして、無機複合酸化物粒子（Ｈ－４）を５０重量％含む硬化体（Ｈ）を調製した。これは、充填材含有率５０重量％、光透過率１０％（５８９ｎｍ）、Ｔｇ１１２℃、熱膨張係数３０ｐｐｍ／℃、吸水率１．８４％であった。

フロントページの続き

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